LLNL-TR-469341

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Reaction Between Thin Gold Wires and Pb-Sn-In Solder (37.5%, 37.5%, 25%), Part C. A comprehensive Model Of The Reaction Inside the Solder Mounds In Both The "Interface Controlled Regime" and The "Diffusion-Controlled" Regime During Long-Term Exposure.

W. J. Siekhaus

February 7, 2011

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Reaction Between Thin Gold Wires And Pb-Sn-In Solder (37.5%, 37.5%, 25%), Part C. A Comprehensive Model Of The Reaction Inside The Solder Mounds In Both The "Interface Controlled Regime" And The "Diffusion-Controlled" Regime During Long-Term Exposure.

Wigbert J. Siekhaus

C.I) Introduction

In part A, all available literature data are displayed in tables, and plotted in figure 1. The slopes of the lines through the data in figure 1 suggest that there is a change in the rate controlling mechanism from interface control (linear with time, slope equals one in figure 1) to diffusion control (proportional to square root of time, slope one half in figure 1) as the gold consumption increases. Here we develop a model for the diffusion controlled reaction using data from planar and circular geometry. We determine the regimes in time and temperature where the reaction is diffusion controlled and where it is interface controlled, and then derive the set of equations for a comprehensive time and temperature dependent model that describes the reaction for all temperatures and time.

C.II) Using all available data to develop a diffusion-controlled reaction model.

The change in mechanism from interface control to diffusion control suggested in figure 1 appears to be temperature dependant. If one extends the line through Yost et al.'s data at 150°C until it intersects the line through the 151°C data of Powell & Braun, one would estimate that this change in rate mechanism occurs at that temperature when the gold consumption is about 50μm. Braun & Rhinehammer's data in figure 1 suggest that at lower temperatures this change in reaction rate control mechanism may occur at gold consumption below 10μm. There are, however, only very few data available that clearly show diffusion control. That makes it difficult to develop a model that can be trusted. To demonstrate the change in the rate controlling mechanism we plot in figure 28 all data of Yost et al.[9], generated in planar geometry. The data of most interest here are the two sets of data at 150°C. (The second set of data at 150°C, shown in figure 14 of Yost et al. are NOT shown in figure 1). There are two points of interest: 1) the data are very reproducible: the filled red triangles (set 1) and the empty purple triangles (set 2) coincide, 2) the data above 10μm show a distinctly different slope (i.e. ½, implying that the reaction in that regime is proportional to square root of time, diffusion controlled.) The linear and non-linear slopes intersect at approximately 20 μm. There is another set of data in planar geometry by Powell and Braun [8]. In figure 29 the data of Powell and Braun are plotted vs. square root of time, together with the 150°C data of Yost et al. The equations fitted to the data are also shown. In order to develop a temperature dependent model for the diffusion controlled reaction the coefficients multiplying "square root of time" should be known over a wide range of temperatures. Unfortunately only one additional set of data for gold consumption above 20μm exists, measured at LLNL for gold wires of 101.6μm diameter at 79.9 and at 90.9 °C, shown in figure 30 as a function of square root of time. Only one single data point exists at 79.9°C. The coefficients multiplying square root of time are calculated or derived in figure 30 (see details there), and used

in figure 31 in an Arrhenius plot to derive the model equation describing the diffusion controlled reaction. As indicated in figure 31, this model equation for the diffusion controlled reaction is generated from only a few data points, and hence subject to revision by additional data.

C III.) Defining the temperature and time regimes where the interface and the diffusion controlled reaction models apply.

Figure 1 already suggests, that the change from interface control to diffusion control is temperature dependent. Figure 29 demonstrates – for temperatures around 150°C - at which time and gold consumption predicted by the linear reaction model intersects the observed square root of time dependent gold consumption. The linear model intersects the data at 142°C at about 22 μm, and the data at 150°C and 151°C at 34 and 55 μm respectively. **Figure 32 shows the intercepts of the linear reaction model and the "square root of time dependent" model at 20, 35, 60 and 150°C. The "square root of time dependent" model derived from the data at elevated temperature (see figure 31) predicts that at 35 and 20°C the reaction may become diffusion controlled for gold consumption less that 10μm. There are no data (see figure 1) that would contradict that prediction. Moreover, Braun and Rhinehammer's data in figure 1 at 70° indicate that a change in reaction mechanism may occur for gold consumption less than 10μm, just as is seen in figure 32 at 60°C. A general equation for deciding whether the reaction is interface controlled or diffusion controlled can be derived by determining the point in temperature and time when the amount of gold converted is the same in both equations, as shown below:**

$$\Delta_{Gold} = A_{Linear}e^{-B_{Linear}/T} * time(month) \; = $$

$$\Delta_{Gold} = A_{SquareRoot}e^{-B_{SquareRoot}/T} * \sqrt{time(month)}$$

With $A_{\text{Linear}} = 1.45 * 10^{10}$, $A_{\text{Square Root}} = 1.5049 * 10^7$

$B_{\text{Linear}} = 7990$, $B_{\text{Square Root}} = 5245.3$

$T(°K) = 273.15 + \text{temperature } °C$

and $\Delta_{\text{Gold}} = \mu m$ of gold consumed

the gold - indium reaction is described by

$$\Delta_{Gold} = A_{Linear} e^{-B_{Linear}/T} * time(month)$$

$$\text{for } \Delta_{Gold} \leq \left(\frac{A_{\text{Square Root}}}{A_{\text{Linear}}}\right)^2 * \left(e^{-\frac{1}{T}\left(B_{SquareRoot} - B_{Linear}\right)}\right)^2$$

$$\Delta_{Gold} = A_{SquareRoot} e^{-B_{SquareRoot}/T} * \sqrt{time(month)}$$

$$\text{for } \Delta_{Gold} \geq \left(\frac{A_{\text{Square Root}}}{A_{\text{Linear}}}\right)^2 * \left(e^{-\frac{1}{T}\left(B_{SquareRoot} - B_{Linear}\right)}\right)^2$$

These equations define a comprehensive time and temperature dependent model for all times and temperatures. A quick look at

C IV.) Summary

We have developed a model for the diffusion controlled reaction, and defined the regime where it applies. It is based on very few data, and hence subject to revision as new data are generated. It predicts a slower rate of gold conversion than the "conservative" interface controlled model. Having defined the regimes where the interface controlled model applies, and where the diffusion controlled model supersedes it, we derive the set of equations of a comprehensive reaction model that applies for all temperatures and times.
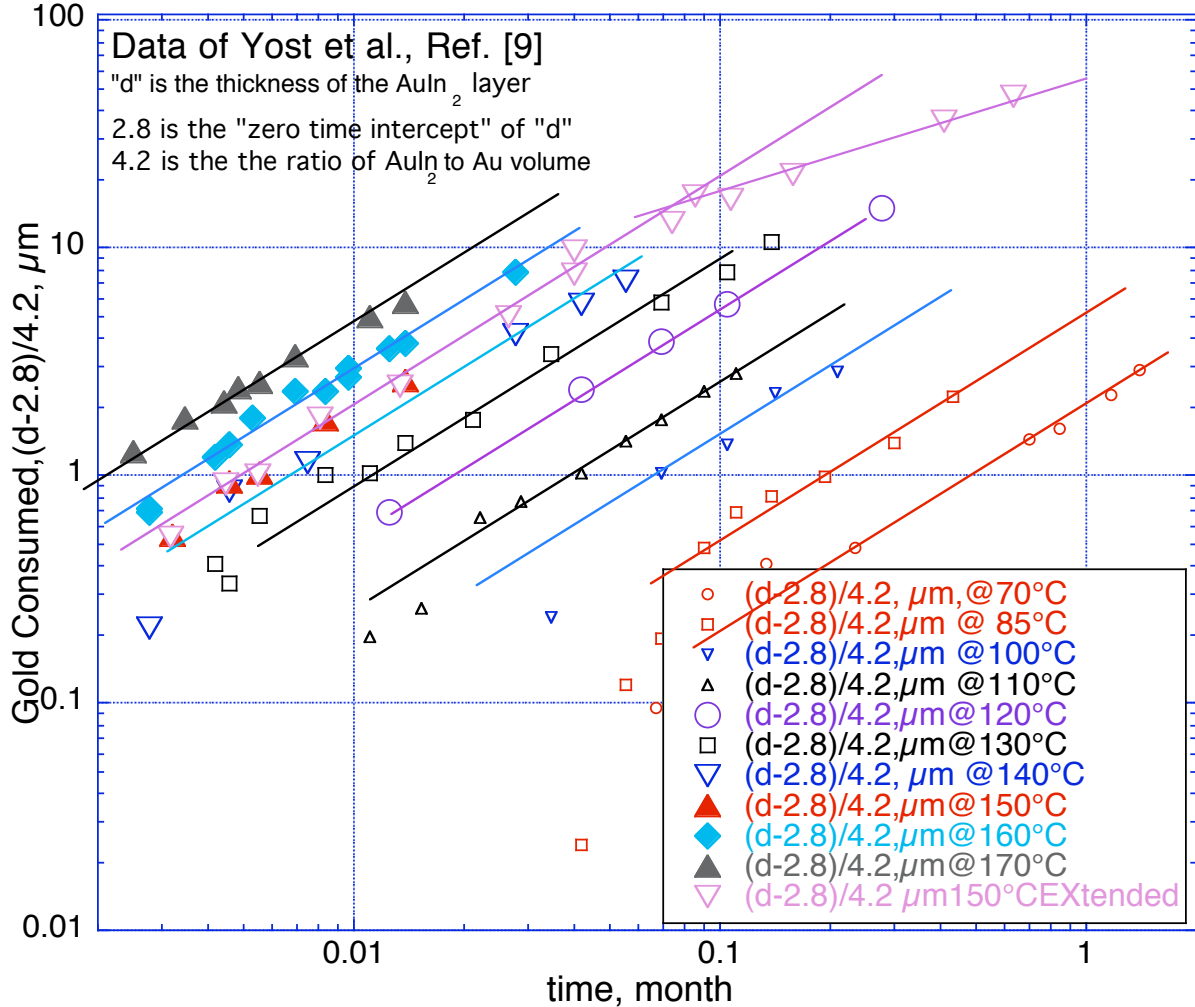
Figure 28. Gold consumption versus time in planar geometry. Data of Yost et al. [9]. The gold consumption is calculated by converting the AuIn₂ thickness observed by Yost et al. to the equivalent of gold. Yost et al.'s "d" data have an "average" zero time intercept of 2.8μm. That "average" intercept is subtracted from the data in this graph, which leads to the deviation from linear behavior for some of the y-axis data below .2μm. The data of most interest here are the two sets of data at 150°C. There are two points of interest: 1) the data are very reproducible: the filled red triangles and the empty purple triangles coincide, 2) the data above about 20μm show a distinctly different slope (i.e. ½, implying that the reaction is proportional to √time, diffusion controlled, in that regime.)
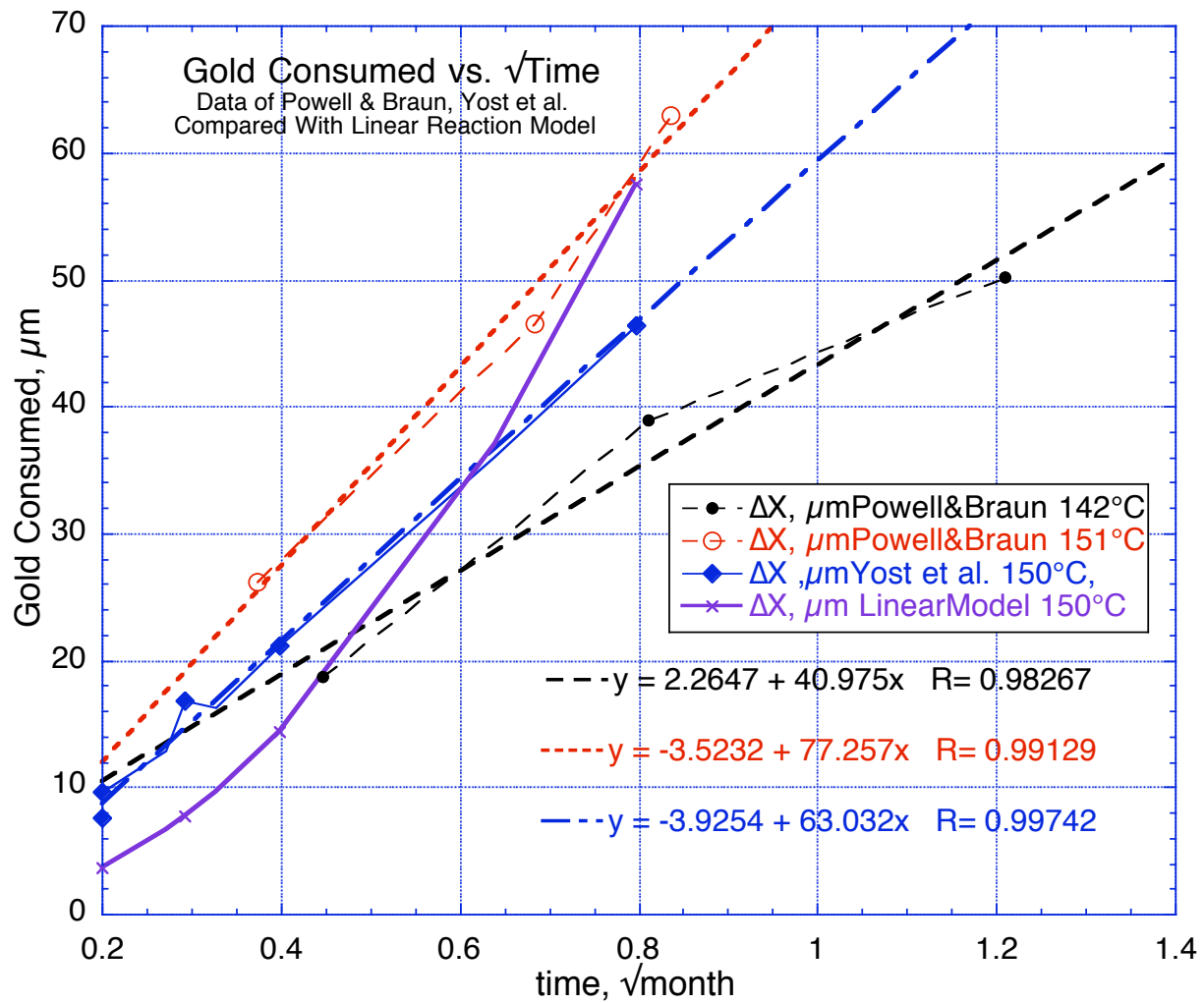
Figure 29. Gold consumption versus square root of time in planar geometry.
Data at 150°C of Yost et al.[9] for gold consumption greater than about 10µm
plotted versus square root of exposure time, together with the data of Powell
and Braun [8] at 142 and 151°C. Both data sets are well fitted with equations
proportional to square root of time, indicating that in this regime the
reaction is diffusion controlled. The rates of reaction per square root of
month are 40.975 at 142°C and 77.257 at 151°C respectively for Powell and
Braun's data, and 63.032 for Yost et al.' data. Also shown is the gold
consumption predicted by the linear reaction model. It intersects the data at
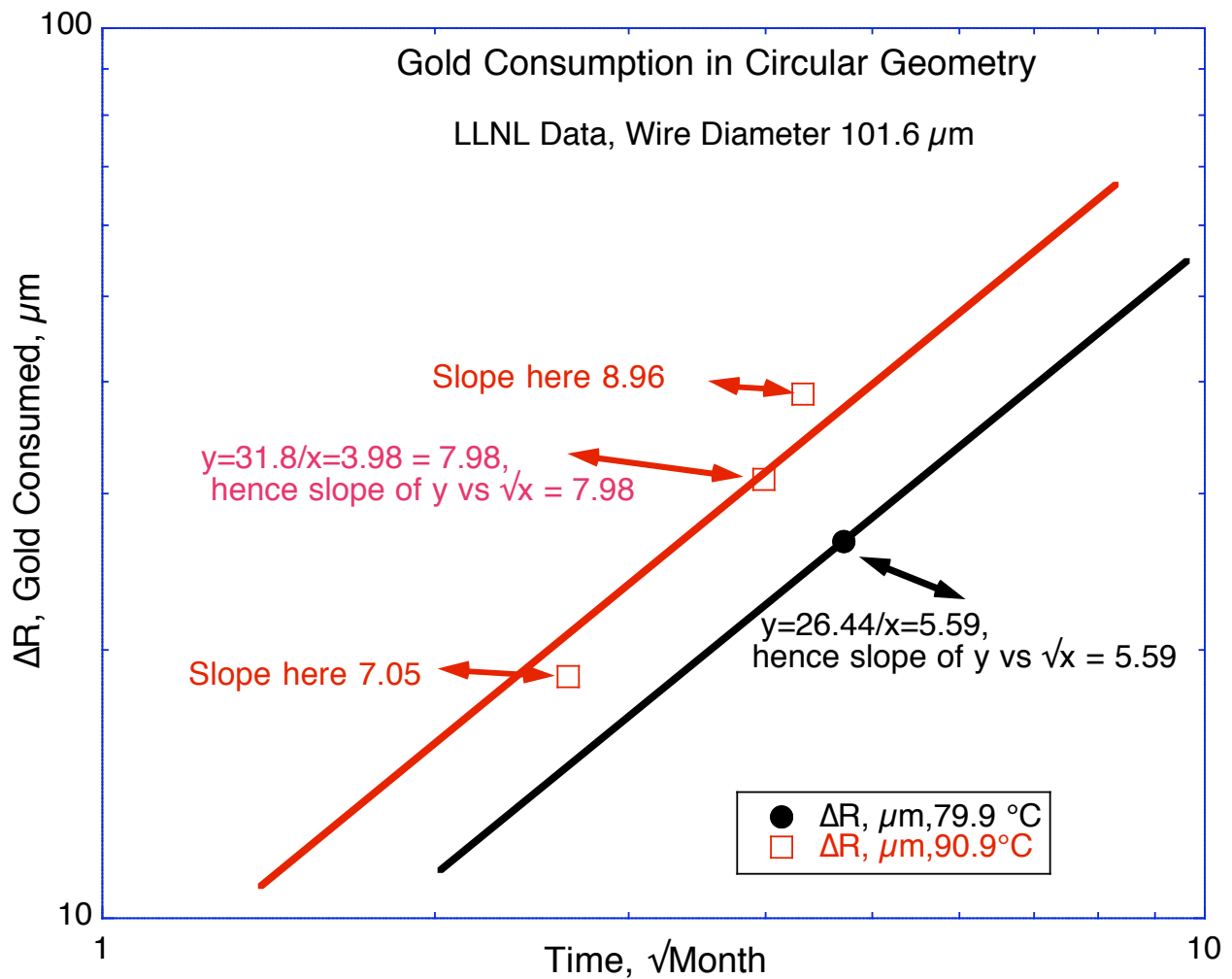142°C at about 22 µm, and the data at 150°C and 151°C at 34 and 55 µm
respectively.

Figure 30. Gold consumption measured at Lawrence Livermore National Laboratory on wires of 101.6 μm diameter plotted in a double logarithmic graph as a function of square root of time. Only one data point exist for 79.9 °C, and only three data points at 90.9°C. Therefore no fit "linear with √time" is done, but rather lines "linear with √time" are drawn in this log-log plot to demonstrate that the measured values are consistent with diffusion control, and the "slopes" are calculated at each data point.
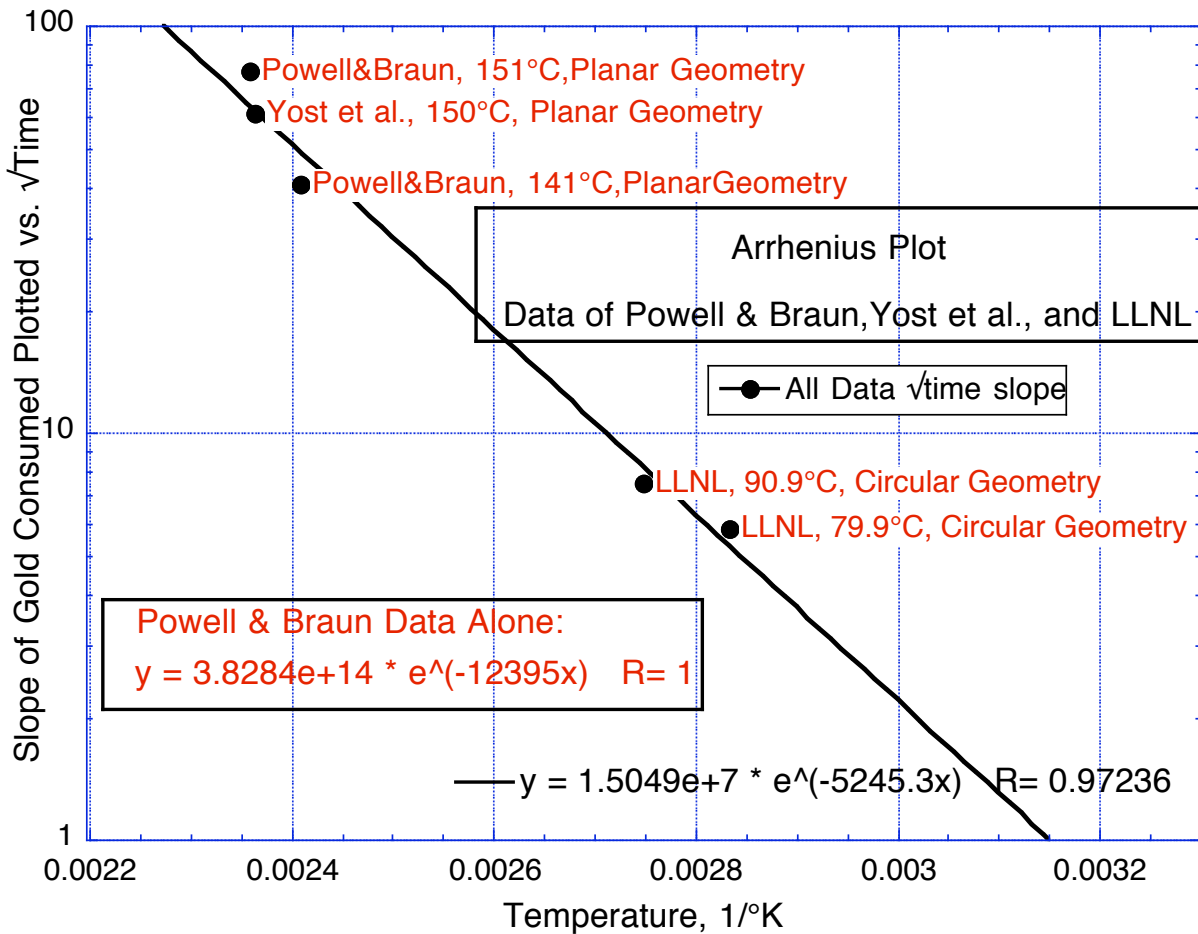
Figure 31. The coefficient multiplying "√time" derived from figures 29 and 30 plotted vs. reciprocal temperature in degree Kelvin. The exponential fit to the data shown in this Arrhenius plot determines the equation describing the rate of the diffusion controlled reaction as a function of time. The activation energy is 5245.3 in units of degree Kelvin, in contrast to the activation energy for the "linear reaction", i.e. 7990, in units of °K. The activation energy determined here is derived from data over a relatively narrow temperature range, using data from planar geometry and from circular geometry. As shown in the graph: if only data of Powell & Braun were used, an activation energy of 12395 (in units of degree Kelvin) would result, with a vastly different pre-exponential factor.
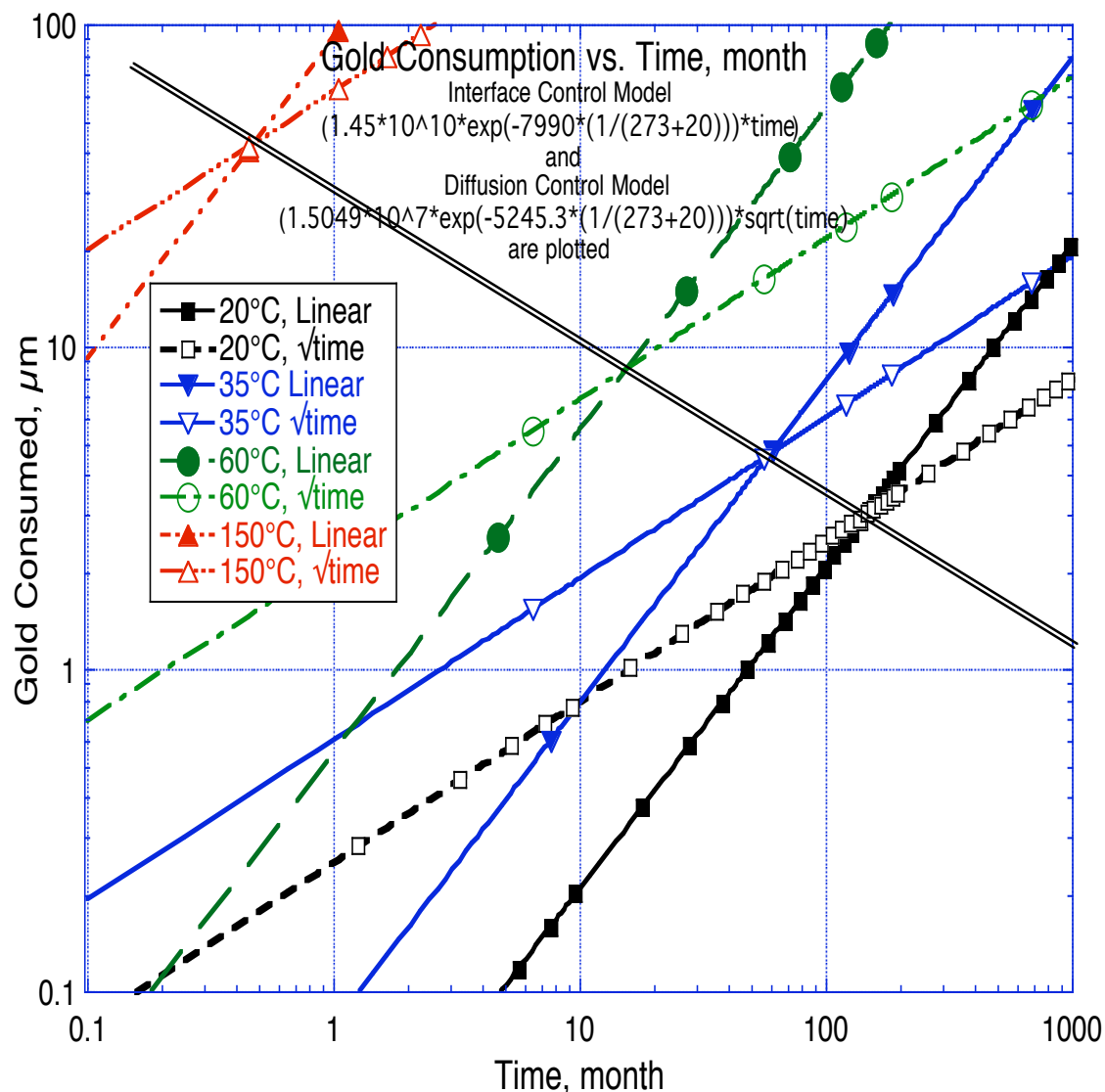
Figure 32. Gold consumption vs. time calculated using both the linear and "√of time" model and showing the intercepts of the linear reaction model and the "square root of time dependent" model at 20, 35, 60 and 150°C. The double line in the graph connects the intersect points. In the region above that line the reaction is diffusion controlled, below that line it is interface controlled. The "square root of time dependent" model derived from the data at elevated temperature predicts that at 35 and 20°C the reaction may become diffusion controlled for gold consumption less that 10μm. There are no data (see figure 1) that would contradict that prediction. Braun and Rhinehammer's data in figure 1 at 70° indicate a change in

reaction mechanism occurs for gold consumption less than 10µm, just as is seen in this figure at 60°C.